

## **Communication: Thermodynamics of condensed matter with strong pressure-energy correlations**

Ingebrigtsen, Trond; Bøhling, Lasse; Schrøder, Thomas; Dyre, J. C.

*Published in:*  
Journal of Chemical Physics

*DOI:*  
[10.1063/1.3685804](https://doi.org/10.1063/1.3685804)

*Publication date:*  
2012

*Document Version*  
Publisher's PDF, also known as Version of record

*Citation for published version (APA):*  
Ingebrigtsen, T., Bøhling, L., Schrøder, T., & Dyre, J. C. (2012). Communication: Thermodynamics of condensed matter with strong pressure-energy correlations. *Journal of Chemical Physics*, 136(6), 061102-1 - 061102-4. <https://doi.org/10.1063/1.3685804>

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain.
- You may freely distribute the URL identifying the publication in the public portal.

### **Take down policy**

If you believe that this document breaches copyright please contact [rucforsk@kb.dk](mailto:rucforsk@kb.dk) providing details, and we will remove access to the work immediately and investigate your claim.

# Communication: Thermodynamics of condensed matter with strong pressure-energy correlations

Trond S. Ingebrigtsen, Lasse Böhling, Thomas B. Schröder, and Jeppe C. Dyre<sup>a)</sup>

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark*

(Received 20 December 2011; accepted 31 January 2012; published online 14 February 2012)

We show that for any liquid or solid with strong correlation between its  $NVT$  virial and potential-energy equilibrium fluctuations, the temperature is a product of a function of excess entropy per particle and a function of density,  $T = f(s)h(\rho)$ . This implies that (1) the system's isomorphs (curves in the phase diagram of invariant structure and dynamics) are described by  $h(\rho)/T = \text{Const.}$ , (2) the density-scaling exponent is a function of density only, and (3) a Grüneisen-type equation of state applies for the configurational degrees of freedom. For strongly correlating atomic systems one has  $h(\rho) = \sum_n C_n \rho^{n/3}$  in which the only non-zero terms are those appearing in the pair potential expanded as  $v(r) = \sum_n v_n r^{-n}$ . Molecular dynamics simulations of Lennard-Jones type systems confirm the theory. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3685804>]

The class of strongly correlating liquids was introduced in Refs. 1 and 2. These liquids are defined by having a correlation coefficient above 0.9 of the constant-volume equilibrium fluctuations of virial  $W$  and potential energy  $U$ . The  $WU$  correlation coefficient varies with state point, but we found from computer simulations that a system has either poor  $WU$  correlations in the entire phase diagram or is strongly correlating at most of its condensed-phase state points.<sup>1–5</sup> Van der Waals and metallic liquids are generally strongly correlating, whereas hydrogen-bonded, ionic, and covalently bonded liquids are generally not. The solid phase is usually at least as strongly correlating as the liquid phase. Theoretical arguments, numerical evidence, and experiments show that strongly correlating liquids are simpler than liquids in general.<sup>1–7</sup>

The simplicity of strongly correlating liquids compared to liquids in general<sup>8</sup> derives from the fact that the former have “isomorphs” in their phase diagram, which are curves of isomorph state points. Two state points with particle density and temperature  $(\rho_1, T_1)$  and  $(\rho_2, T_2)$  are termed *isomorphic*<sup>3</sup> if all pairs of physically relevant microconfigurations of the state points that trivially scale into one another (i.e.,  $\rho_1^{1/3} \mathbf{r}_i^{(1)} = \rho_2^{1/3} \mathbf{r}_i^{(2)}$  for all particles  $i$ ) have proportional configurational Boltzmann factors:

$$e^{-U(\mathbf{r}_1^{(1)}, \dots, \mathbf{r}_N^{(1)})/k_B T_1} = C_{12} e^{-U(\mathbf{r}_1^{(2)}, \dots, \mathbf{r}_N^{(2)})/k_B T_2}. \quad (1)$$

Only inverse-power-law liquids<sup>9</sup> have exact isomorphs (here  $C_{12} = 1$ ), but as shown in Appendix A of Ref. 3 a system is strongly correlating if and only if it has isomorphs to a good approximation.

The invariance of the canonical probabilities of scaled microconfigurations along an isomorph has several implications, for instance:<sup>1–3</sup> (1) the excess entropy and the isochoric specific heat are isomorph invariants, (2) the reduced-unit dynamics is isomorph invariant for both Newtonian and stochas-

tic dynamics, (3) all reduced-unit static correlation functions are isomorph invariant, and (4) a jump between isomorph state points takes the system instantaneously to equilibrium. Using reduced units means measuring length in terms of the unit  $\rho^{-1/3}$  and time in units of  $\rho^{-1/3} \sqrt{m/k_B T}$  where  $m$  is the average particle mass. Since isomorphs are generally approximate, isomorph properties are likewise rarely rigorously obeyed.

All thermodynamic quantities considered below are excess quantities, i.e., in excess of those of an ideal gas at the same density and temperature. Thus,  $S$  is the *excess* entropy ( $S < 0$ ),  $C_V$  is the *excess* isochoric specific heat,  $p$  is the *excess* pressure (i.e.,  $p = W/V$ ), etc.

Briefly, the reason that  $S$  and  $C_V$  are isomorph invariants is the following.<sup>3</sup> The entropy is determined by the canonical probabilities, which are identical for scaled microconfigurations of two isomorph state points. From Einstein's formula  $C_V = \langle (\Delta U)^2 \rangle / k_B T^2$  the isomorph invariance of  $C_V$  follows easily by taking the logarithm of Eq. (1) and making use of the isomorph invariance of scaled microconfiguration probabilities.

Since  $S$  and  $C_V$  are invariant along the same curves in the phase diagram,  $C_V$  is a function of  $S$ :  $C_V = \phi(S)$ . Thus,  $T(\partial S / \partial T)_V = \phi(S)$  or at constant volume:  $dS/\phi(S) = dT/T$ . Integrating this leads to an expression of the form  $\psi(S) = \ln(T) + k(V)$ , which implies  $T = \exp[\psi(S)] \exp[-k(V)]$ . The generic version of this involves only intensive quantities ( $s \equiv S/N$ ):

$$T = f(s)h(\rho). \quad (2)$$

For inverse-power-law interactions ( $\propto r^{-n}$ ) the entropy is well known to be a function of  $\rho^\gamma/T$  where  $\gamma = n/3$ :  $S = K(\rho^\gamma/T)$ . Applying the inverse of the function  $K$  shows that these perfectly correlating systems obey Eq. (2) with  $h(\rho) = \rho^\gamma$ .

The thermodynamic separation identity Eq. (2) is the main result of this communication. We proceed to discuss some consequences and numerical tests.

<sup>a)</sup>Electronic mail: dyre@ruc.dk.

**Density scaling:** Since entropy is an isomorph invariant, it follows from Eq. (2) that the variable characterizing an isomorph may be chosen as  $h(\rho)/T$ . In particular, the reduced relaxation time  $\tilde{\tau}$ , which is also an isomorph invariant, may be written for some function  $G$ :

$$\tilde{\tau} = G\left(\frac{h(\rho)}{T}\right). \quad (3)$$

This is the form of “density scaling” proposed by Alba-Simionesco *et al.* in 2004 from different arguments;<sup>10</sup> at the same time Dreyfus *et al.*, as well as Casalini and Roland, favored the more specific form  $\tilde{\tau} = G(\rho^\gamma/T)$ .<sup>10</sup> Isochrones for many supercooled liquids and polymers follow to a good approximation the latter “power-law density scaling” relation.<sup>11</sup> For large density changes, however, it was recently shown that the density-scaling exponent varies significantly in both simulations and experiments;<sup>12</sup> these cases conform to the more general equation (3).

**An expression for the density-scaling exponent:** The general, state-point dependent density-scaling exponent  $\gamma$  is defined<sup>2,3</sup> by

$$\gamma \equiv \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_S = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_\tau. \quad (4)$$

The physical interpretation of Eq. (4) is the following. If density is increased by 1%, temperature should be increased by  $\gamma\%$  for the system to have the same entropy and reduced relaxation time. Equation (2) implies  $d \ln T = d \ln f(S) + d \ln h(\rho)$ ; thus along an isomorph one has  $d \ln T = d \ln h$ . Via Eq. (4) this implies

$$\gamma = \frac{d \ln h}{d \ln \rho}. \quad (5)$$

In particular,  $\gamma$  depends only on density:  $\gamma = \gamma(\rho)$ .<sup>3</sup>

**Configurational Grüneisen equation of state:** The Grüneisen equation of state expresses that pressure equals a density-dependent number times energy plus a term that is a function of density only.<sup>13</sup> This equation of state is used routinely for describing condensed matter at high pressures and temperatures. We proceed to show that strongly correlating systems obey the configurational version of the Grüneisen equation of state, which as suggested by Casalini *et al.*<sup>14</sup> has the density-scaling exponent as the proportionality constant:<sup>3,4</sup>

$$W = \gamma(\rho)U + \Phi(\rho). \quad (6)$$

To prove this, note first that  $(\partial U/\partial S)_\rho = T = f(S)h(\rho)$  by integration implies  $U = F(S)h(\rho) + k(\rho)$  where  $F'(S) = f(S)$  ( $S$  is the extensive entropy). Since  $W = (\partial U/\partial \ln \rho)_S$  (which follows from the standard identity  $TdS = dU + pdV$ ), we get  $W = F(S)dh/d \ln \rho + dk/d \ln \rho$ . Substituting into the latter expression  $F(S)$  isolated from  $U = F(S)h(\rho) + k(\rho)$  leads to Eq. (6), in which  $\gamma(\rho)$  is given by Eq. (5). It is straightforward to show that, conversely, Eq. (6) implies the thermodynamic separation identity Eq. (2).

**The isomorphs of atomic systems:** We consider now predictions for systems of “atomic” particles interacting via pair potentials of the form<sup>15</sup> (where  $r$  is the distance between two

particles)

$$v(r) = \sum_n v_n r^{-n}. \quad (7)$$

For simplicity only the case of identical particles is considered, but the arguments generalize trivially to multicomponent systems. Consider the thermal average  $\langle r^{-n} \rangle$ . Switching to reduced units defined by  $\tilde{r} \equiv \rho^{1/3}r$ , we have  $\langle r^{-n} \rangle = \langle \tilde{r}^{-n} \rangle \rho^{n/3}$ . Since structure is isomorph invariant in reduced units,  $\langle \tilde{r}^{-n} \rangle$  is an isomorph invariant. Consequently, it is a function of any other isomorph invariant, for instance the entropy:  $\langle \tilde{r}^{-n} \rangle = G_n(S)$ . Noting that the average potential energy is a sum of Eq. (7) over all particle pairs, we conclude that (where  $H_n(S) \propto v_n G_n(S)$ )

$$U = \sum_n H_n(S) \rho^{n/3}. \quad (8)$$

Taking the derivative of this equation with respect to temperature at constant volume leads to

$$\left(\frac{\partial U}{\partial T}\right)_V = \sum_n H'_n(S) \left(\frac{\partial S}{\partial T}\right)_V \rho^{n/3}. \quad (9)$$

The left-hand side is  $T(\partial S/\partial T)_V$ , so Eq. (9) implies

$$T = \sum_n H'_n(S) \rho^{n/3}. \quad (10)$$

This is consistent with the thermodynamic separation identity Eq. (2) only if all the functions  $H'_n(S)$  are proportional to some function, i.e., if one can write  $H'_n(S) = C_n \phi(S)$ . We identify  $\phi(S)$  as the function  $f(S)$  of Eq. (2), which means that

$$h(\rho) = \sum_n C_n \rho^{n/3}. \quad (11)$$

Thus, for strongly correlating atomic liquids, the thermodynamic function  $h(\rho)$  has an analytical structure, which is inherited from  $v(r)$  in the sense that the only non-zero terms of  $h(\rho)$  are those corresponding to non-zero terms of  $v(r)$ . Note that not all systems with potentials of Eq. (7) are strongly correlating and that the derivation applies only if this is the case.

As an illustration we present results from *NVT* simulations of the Kob-Andersen binary Lennard-Jones (KABLJ) liquid,<sup>16</sup> which is strongly correlating at its condensed-phase state points.<sup>1-3</sup> The application of the above to LJ systems predicts that  $H'_{12}(S) \propto H'_6(S)$ , where  $H_{12}(S)$  is the reduced coordinate average of the  $r^{-12}$  term of  $U$ . Integrating this leads to  $H_{12}(S) = \alpha H_6(S) + \beta$ , implying that if the repulsive term in  $U$  is plotted against the attractive term in reduced units, all points are predicted to fall onto a common line. Figure 1 presents data where density was changed by a factor of eight and temperature by a factor of 40 000. The data collapse is good but not exact, which reminds us that the relations derived are approximate.

The theory implies a simple mathematical description of the isomorphs in the  $(\rho, T)$  phase diagram. From the fact that the potential energy contains only  $r^{-12}$  and  $r^{-6}$  terms, it follows that  $h(\rho) = A\rho^4 - B\rho^2$ . Consequently, LJ isomorphs are given by

$$\frac{A\rho^4 - B\rho^2}{T} = \text{Const.} \quad (12)$$

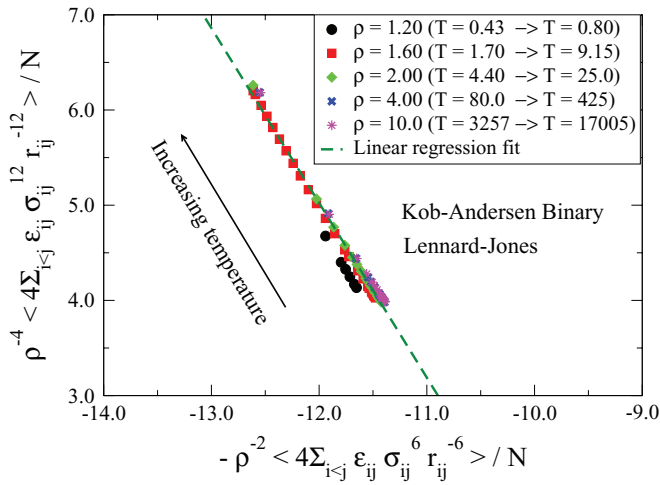


FIG. 1. The thermal average of  $r^{-12}$  versus that of  $-r^{-6}$  in reduced units for a large range of state points of the Kob-Andersen binary Lennard-Jones liquid simulated with 1000 particles ( $\epsilon_{AA} = \sigma_{AA} = 1$ ). These quantities correspond to  $H_{12}(S)$  and  $H_6(S)$  in Eq. (8). The theory predicts that  $H'_{12}(S) \propto H'_6(S)$ , implying that all data points should fall onto a common line according to  $H_{12}(S) = \alpha H_6(S) + \beta$ .

The invariance of the Boltzmann statistical weights of scaled microconfigurations implies that an isomorph cannot cross the liquid-solid coexistence curve. In particular, the coexistence curve is itself predicted to be an isomorph,<sup>3</sup> which was recently confirmed by simulations of generalized LJ liquids.<sup>4,17</sup> Consequently, the coexistence line is given by Eq. (12). This validates a recent conjecture of Khrapak and Morfill.<sup>18</sup>

**Predictions for the repulsive Lennard-Jones fluid:** As a final illustration we consider the “repulsive” single-component LJ fluid defined by the pair potential  $v(r) = (r^{-12} + r^{-6})/2$ , a system with  $WU$  correlation coefficient above 99.9% in its entire phase diagram. At low densities ( $\rho \ll 1$ ) the repulsive LJ fluid behaves as an  $r^{-6}$  fluid, whereas it for  $\rho \gg 1$  is effectively an  $r^{-12}$  fluid. Thus, the density-scaling exponent  $\gamma(\rho)$  varies from 2 to 4 as density increases, a much larger variation than that of previously studied strongly correlating systems.

Since  $h(\rho)$  is only defined within an overall multiplicative constant, one can write for the repulsive LJ fluid  $h(\rho) = \alpha\rho^4 + (1-\alpha)\rho^2$ . This leads via Eq. (5) to  $\gamma_0 = 2 + 2\alpha$ , where  $\gamma_0$  is the density-scaling exponent at reference density unity, implying that

$$h(\rho) = (\gamma_0/2 - 1)\rho^4 + (2 - \gamma_0/2)\rho^2. \quad (13)$$

Our simulations identified from the expression  $\gamma_0 = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$  (Ref. 3) the exponent  $\gamma_0 = 3.56$  at the state point  $(\rho, T) = (1, 1)$ . Equation (13) with  $\gamma_0 = 3.56$  was tested in two different ways. First, we compared at each state point along an isomorph the exponent  $\gamma(\rho)$  predicted from Eqs. (5) and (13) with that calculated from the fluctuations via  $\gamma = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$  (right panel of Fig. 2). The left panel presents a second test of Eq. (13) by showing results from simulating five temperatures at  $\rho = 1$ , plotting for each temperature instantaneous values of the potential energy versus the potential energy of the same microconfigurations scaled to three other densities ( $\rho = 0.5, 1.6, 2.0$ ). The theory behind the observed straight lines is

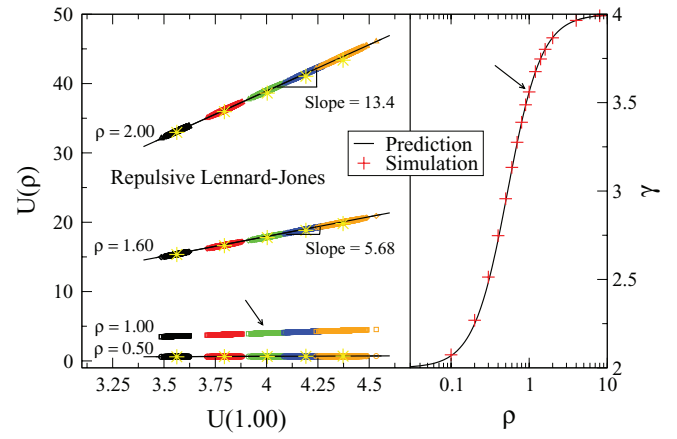


FIG. 2. “Multiple direct isomorph check” applied to simulations of  $N = 1000$  particles of the repulsive LJ fluid defined by the pair potential  $(r^{-12} + r^{-6})/2$ . The left panel shows a scatter plot of the potential energies of pairs of microconfigurations, where the potential energy of a given microconfiguration at density 1.0 is denoted  $U(1.00)$  and that of the same microconfiguration scaled to density  $\rho$  is denoted  $U(\rho)$  ( $\rho = 0.5, 1.6, 2.0$ ). This was done for  $T = 0.6, 0.8, 1.0, 1.2, 1.4$ . The yellow asterisks mark the average of each scatter plot. The black lines are the predictions (see the text) with slopes determined via Eq. (13) from the fluctuations calculated at the state point  $(\rho, T) = (1, 1)$  marked by an arrow. The right panel shows the density-scaling exponent along an isomorph predicted from Eqs. (5) and (13) (full curve) and the exponent calculated at each state point from the fluctuation formula  $\gamma = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$  (Ref. 3) (red crosses). The arrow marks the state point  $(\rho, T) = (1, 1)$ .

the following. Consider two isomorph state points  $(\rho_0, T_0)$  and  $(\rho, T)$  and suppose each temperature is changed a little, keeping both densities constant. If the two new state points are also isomorphic, the entropy change is the same for both:  $dU_0/T_0 = dU/T$ . This implies  $dU/dU_0 = T/T_0$ , i.e.,  $(\partial U / \partial U_0)_{\rho_0, \rho} = T/T_0$ . Since  $h(\rho)/T$  is constant along an isomorph, this implies  $(\partial U / \partial U_0)_{\rho_0, \rho} = h(\rho)/h(\rho_0)$ . Integrating this at constant  $\rho_0$  and  $\rho$  leads to  $U = [h(\rho)/h(\rho_0)]U_0 + \phi(\rho_0, \rho)$ . In our case of reference density unity  $\rho_0 = 1$  and  $h(\rho_0) = 1$ . Thus, plotting  $U$  versus  $U_0$  is predicted to result in straight lines with slope  $h(\rho)$  (yellow asterisks in the left panel of Fig. 2). The scaled state points are isomorphic to the original  $\rho = 1$  state points, with temperatures given by  $T = T_0 h(\rho)$ . Via the “direct isomorph check”<sup>3</sup> this implies that the scaled microconfigurations form elongated ovals also with slope  $h(\rho)$ .

In summary, we have shown that for strongly correlating liquids or solids, temperature separates into a function of entropy times a function of density. For these systems the energy scale is consequently determined by density alone. It is an open question whether, conversely, the thermodynamic separation identity equation (2) implies that the system in question is strongly correlating. We anticipate that this is the case, at least for realistic potentials.

The centre for viscous liquid dynamics “Glass and Time” is sponsored by the Danish National Research Foundation (DNRF).

<sup>1</sup>N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schröder, and J. C. Dyre, *J. Chem. Phys.* **128**, 184507 (2008); N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schröder, and J. C. Dyre, *ibid.* **129**, 184508 (2008); T. B. Schröder,

- N. P. Bailey, U. R. Pedersen, N. Gnan, and J. C. Dyre, *ibid.* **131**, 234503 (2009).
- <sup>2</sup>U. R. Pedersen, N. P. Bailey, T. B. Schröder, and J. C. Dyre, *Phys. Rev. Lett.* **100**, 015701 (2008); N. Gnan, C. Maggi, T. B. Schröder, and J. C. Dyre, *ibid.* **104**, 125902 (2010); U. R. Pedersen, T. B. Schröder, and J. C. Dyre, *ibid.* **105**, 157801 (2010).
- <sup>3</sup>N. Gnan, T. B. Schröder, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, *J. Chem. Phys.* **131**, 234504 (2009).
- <sup>4</sup>T. B. Schröder, N. Gnan, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, *J. Chem. Phys.* **134**, 164505 (2011).
- <sup>5</sup>U. R. Pedersen, N. Gnan, N. P. Bailey, T. B. Schröder, and J. C. Dyre, *J. Non-Cryst. Solids* **357**, 320 (2011).
- <sup>6</sup>D. Gundermann, U. R. Pedersen, T. Hecksher, N. P. Bailey, B. Jakobsen, T. Christensen, N. B. Olsen, T. B. Schröder, D. Fragiadakis, R. Casalini, C. M. Roland, J. C. Dyre, and K. Niss, *Nat. Phys.* **7**, 816 (2011).
- <sup>7</sup>T. S. Ingebrigtsen, T. B. Schröder, and J. C. Dyre, e-print arXiv:1111.3557 (2011).
- <sup>8</sup>O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954); J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980); J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982); M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford Science Publications, Oxford, 1987); D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, New York, 1987); P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University, Princeton, NJ, 1996); N. H. March and M. P. Tosi, *Introduction to Liquid State Physics* (World Scientific, Singapore, 2002); J.-L. Barrat and J.-P. Hansen, *Basic Concepts for Simple and Complex Liquids* (Cambridge University Press, Cambridge, England, 2003); J.-P. Hansen and J. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic, New York, 2005).
- <sup>9</sup>O. Klein, *Medd. Vetenskapsakad. Nobelinst.* **5**, 1 (1919); T. H. Berlin and E. W. Montroll, *J. Chem. Phys.* **20**, 75 (1952); W. G. Hoover, M. Ross, K. W. Johnson, D. Henderson, J. A. Barker, and B. C. Brown, *ibid.* **52**, 4931 (1970); W. G. Hoover, S. G. Gray, and K. W. Johnson, *ibid.* **55**, 1128 (1971); Y. Hiwatari, H. Matsuda, T. Ogawa, N. Ogita, and A. Ueda, *Prog. Theor. Phys.* **52**, 1105 (1974); D. M. Heyes and A. C. Branka, *J. Chem. Phys.* **122**, 234504 (2005); A. C. Branka and D. M. Heyes, *Phys. Rev. E* **74**, 031202 (2006).
- <sup>10</sup>C. Alba-Simionesco, D. Kivelson, and G. Tarjus, *J. Chem. Phys.* **116**, 5033 (2002); C. Dreyfuss, A. Aouadi, J. Gapinski, M. Matos-Lopes, W. Steffen, A. Patkowski, and R. M. Pick, *Phys. Rev. E* **68**, 011204 (2003); C. Alba-Simionesco, A. Cailliaux, A. Alegria, and G. Tarjus, *Europhys. Lett.* **68**, 58 (2004); R. Casalini and C. M. Roland, *Phys. Rev. E* **69**, 062501 (2004).
- <sup>11</sup>C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, *Rep. Prog. Phys.* **68**, 1405 (2005); G. Floudas, M. Paluch, A. Grzybowski, and K. L. Ngai, *Molecular Dynamics of Glass-Forming Systems: Effects of Pressure* (Springer, New York, 2010); D. Fragiadakis and C. M. Roland, *J. Chem. Phys.* **134**, 044504 (2011).
- <sup>12</sup>L. Bøhling, T. S. Ingebrigtsen, A. Grzybowski, M. Paluch, J. C. Dyre, and T. B. Schröder, e-print arXiv:1112.1602 (2011).
- <sup>13</sup>M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, U.K., 1954); M. Ross and D. A. Young, *Annu. Rev. Phys. Chem.* **44**, 61 (1993); L. Burakovsky and D. L. Preston, *J. Phys. Chem. Solids* **65**, 1581 (2004).
- <sup>14</sup>R. Casalini, U. Mohanty, and C. M. Roland, *J. Chem. Phys.* **125**, 014505 (2006).
- <sup>15</sup>Y. Rosenfeld, *Phys. Rev. A* **26**, 3633 (1982).
- <sup>16</sup>W. Kob and H. C. Andersen, *Phys. Rev. Lett.* **73**, 1376 (1994).
- <sup>17</sup>A. Ahmed and R. J. Sadus, *J. Chem. Phys.* **131**, 174504 (2009).
- <sup>18</sup>S. A. Khrapak and G. E. Morfill, *J. Chem. Phys.* **134**, 094108 (2011).